Provenance of metalliferous mudstones associated with the Lemarchant volcanogenic massive sulphide (VMS) deposit, central Newfoundland, Canada: Insights from Nd isotopes and lithogeochemistry

Stefanie Lode[1*], Stephen J. Piercey[1], Jonathan Cloutier[2]

[1]*Department of Earth Sciences, Memorial University, 300 Prince Philip Drive, St. John's, NL, Canada, A1B 3X5*

[2]*Department of Earth Sciences, University of St. Andrews, St. Andrews, Scotland, UK, KY16 9AL*

**Correspondence (slode@mun.ca)*

Abstract: Neodymium isotope data on metalliferous mudstones (exhalites) and tuffs from the Cambrian Lemarchant VMS deposit provide insights into the tectonic environment of the Tally Pond volcanic belt, Canada. The Lemarchant samples have εNd_{513} = −6.0 to −1.8, whereas associated volcanic rocks have εNd_{513} of +0.4 to +1.4. The more evolved values in the exhalites have not been reported yet; however, they overlap the εNd of the underlying Ganderian Neoproterozoic Sandy Brook Group (εNd_t = −6.5 to −1.9), and Crippleback Intrusive Suite (εNd_t = −5.9 to −5.2). The evolved Nd isotopic signatures suggest that the Tally Pond volcanic belt was formed upon Ganderian arc basement, which itself was possibly built upon, or proximal to, the Gondwanan

Amazonian margin. Erosion of older crustal material and Tally Pond volcanic belt volcanic rocks, together with coeval eruption of the volcanic rocks, released Nd-rich detritus into the water column. Uptake of eroded detrital and scavenged Nd resulted in mixed Nd sources (juvenile and evolved), archived in the exhalites. The results of this study are of significance not only for occurrences of exhalites within the Tally Pond volcanic belt, but also have exploration implications for VMS districts globally.

Metalliferous mudstones (exhalites) are abundant in the Tally Pond volcanic belt, central Newfoundland Appalachians, Canada, and are locally genetically associated with volcanogenic massive sulphide (VMS) deposits (Swinden 1991; Squires & Moore 2004). The Tally Pond volcanic belt, which is part of the Dunnage Zone, Newfoundland, Canada, belongs to the Cambrian (~515 Ma) to Permian (~275 Ma) Appalachian-Caledonide mountain belt that hosts numerous VMS deposits, including the past-producing Duck Pond and Boundary mines, and the precious metal-bearing Lemarchant deposit (Fig. 1A-B; Williams 1979; Swinden 1988, 1991; Evans & Kean 2002; Grenne & Slack 2003; Rogers *et al*. 2007; van Staal &Barr 2011; Piercey *et al*. 2014; Hollis *et al*. 2015). The Tally Pond group (~513-509 Ma) volcanic rocks and related massive sulphide mineralization formed during arc rifting during the construction of the Cambrian to Early Ordovician Penobscot Arc, which is known to be built upon Ganderian Neoproterozoic (~563 Ma) arc basement of the Crippleback Intrusive Suite and the coeval Sandy Brook Group (Pollock *et al*. 2002; Zagorevski *et al*. 2007; Zagorevski *et al*. 2010; Piercey *et al*.

2014). In the Neoproterozoic and Early Cambrian Ganderia was located north-west of the Gondwanan Amazonian margin (Fyffe *et al*. 2009; van Staal *et al*. 2012; Murphy *et al*. 2014). The Penobscot arc represented the leading edge of Ganderia in a supra-subduction zone setting and arc rifting was initiated due to slab roll-back along this margin (Jenner & Swinden 1993; Schulz *et al*. 2008; Murphy *et al*. 2014). The basement to the Ganderian arc is not exposed; however, detrital zircon and Nd isotopic studies indicate the presence of older crustal rocks that were derived from the Gondwanan Amazonian craton (Nance *et al*. 2008; Schulz *et al*. 2008). Rifting of the Penobscot Arc led to the formation of volcanogenic massive sulphide (VMS) mineralization and associated hydrothermal sedimentary rocks of the Tally Pond group (Rogers *et al*. 2006; Copeland *et al*. 2009; Zagorevski *et al*. 2010; Piercey *et al*. 2014; Lode *et al*. 2016).

During rifting of the Penobscot arc there was extension, massive sulfide formation, and the genesis of hydrothermal sedimentary rocks that formed from the deposition from buoyant hydrothermal plumes from black smokers (Hekinian *et al*. 1993; Hannington *et al*. 1995; German & Von Damm 2003). These black smokers and associated hydrothermal sedimentary rocks occur where hydrothermal fluids are focused along deep synvolcanic faults in extensional settings (e.g., ocean ridges, rifted arcs, or backarc basin spreading centres) (Fig. 2; Lydon 1984; Hannington *et al*. 2005; Gibson *et al*. 2007). The hydrothermal fluids consist of modified seawater, which is entrained through oceanic or rift-related continental crust, and are variably metal bearing with Fe, Mn, Cu, Pb, and Zn, as well as reduced sulphur and Si (Von Damm 1990; German & Von Damm 2003; Galley *et al*. 2007; Tivey 2007; Huston *et al*. 2010). The metals and other ligands are generally derived from seawater (S) and leached from host rocks (e.g., metals, Si±S) (Fig.

2; Hannington *et al*. 2005; Huston *et al*. 2011). Hydrothermal plume-derived Fe-oxyhydroxides are efficient scavengers of trace metals (e.g., oxyanions such as HPO_4^{2-}, HVO_4^{2-}, CrO_4^{2-}, $HAsO_4^{2-}$) and rare earth elements (REE) plus Y from seawater (Mills & Elderfield 1995; Rudnicki 1995). A rifted arc environment exposes rock units of different ages, hence varying Nd isotopic signatures, which contribute detrital material to the hydrothermal matter in the exhalative sedimentary rocks due to erosional and weathering processes (Keto & Jacobson 1988; Mills & Elderfield 1995). Therefore, exhalites not only record seawater REE (including Nd) but also the provenance components of the detrital sources at the time of formation (Mills & Elderfield 1995; Peter 2003; Lode *et al*. 2015).

By using various isotopic tracers, such as Nd isotopes, it is possible to decipher the potential sources of various components in hydrothermal sedimentary rocks. The Nd isotopic system is specifically useful for understanding the relative roles of evolved versus juvenile crust, and provides further insight into the tectonic environment and provenance of the metalliferous mudstones, as it is robust and not significantly modified by diagenetic, hydrothermal, and metamorphic processes (McCulloch & Wasserburg 1978; McLennan *et al*. 2003). In addition, the separation of Sm-Nd in Earth's reservoirs is particularly useful in delineating juvenile versus evolved crust and the time-integrated sources of materials in Earth materials (McCulloch & Wasserburg 1978; Rollinson 1993; McLennan *et al*. 2003). The Tally Pond belt volcanic rocks have εNd signatures that are typically positive, whereas their basement rocks, i.e., the rifted arc rocks of the Neoproterozoic Crippleback Intrusive Suite and the Sandy Brook Group show more evolved εNd values (McLennan *et al*. 1993; Rogers *et al*. 2006; Nance *et al*. 2008;

McNicoll *et al*. 2010; Piercey *et al*. 2014). Given the level of preservation of stratigraphy of the lithofacies in the Lemarchant deposit, including the metalliferous mudstones, this deposit is an excellent location to understand the provenance of hydrothermal mudstones in ancient rifted arcs. Correspondingly, the Nd isotopic signatures in the mudstones may be useful in outlining their provenance and the potential contributions of local versus basement versus distal sources in their genesis.

The purpose of this study is to: 1) determine the sources of Nd in the metalliferous mudstones and massive sulphides of the Lemarchant deposit; and 2) because the Tally Pond volcanic belt is formed upon Ganderian and possibly older basement rocks, to evaluate the relative roles of mantle and evolved crustal inputs that contributed to the Lemarchant hydrothermal sedimentary rocks using the Nd isotope compositions of metalliferous mudstones.

Regional Geology

The Tally Pond volcanic belt is located within the Central Mobile Belt, Newfoundland, Canada, which is part of the Cambrian (~515 Ma) to Permian (~275 Ma) Appalachian mountain belt (Williams 1979; Swinden 1988; Rogers *et al*. 2007; van Staal & Barr 2011). The Newfoundland Appalachians are divided into four tectonostratigraphical zones (from west to east): Humber, Dunnage, Gander and Avalon zones (Fig. 1A; Williams 1979; Swinden 1988, 1991). The Dunnage Zone represents the Central Mobile Belt (Williams *et al*. 1988; Swinden 1991; Rogers *et al*. 2007). These zones result from and were affected by the successive accretion of three micro-continental blocks during the Early Palaeozoic to Middle Palaeozoic (i.e., Dashwoods, Taconic orogenesis;

Ganderia, Salinic orogenesis; and Avalonia, Acadian orogenesis) and related interoceanic arcs and backarcs (Swinden 1991; Zagorevski *et al*. 2010). In the Palaeozoic (Middle Cambrian to Ordovician), these ribbon-shaped micro-continental blocks separated from Gondwana and Laurentia, forming peri-Gondwanan and peri-Laurentian terranes and subsequently accreted to Laurentia creating the composite Laurentian margin (Rogers *et al*. 2007; Zagorevski *et al*. 2010; van Staal & Barr 2011). The Exploits Subzone represents two phases of arc-backarc formation, the Cambrian to Early Ordovician Penobscot Arc and the Early to Middle Ordovician Victoria Arc (Zagorevski *et al*. 2010). The Tally Pond volcanic belt and its VMS deposits (Duck Pond and Boundary mines; Lemarchant deposit; Fig. 1B) are hosted in the lower Victoria Lake supergroup within the Exploits Subzone, which is comprised of Cambrian to Ordovician volcanic and sedimentary rocks (Dunning *et al*. 1991; Rogers *et al*. 2007; McNicoll *et al*. 2010; van Staal & Barr 2011). The Victoria Lake supergroup is further subdivided into six assemblages (Zagorevski *et al*. 2010; Piercey *et al*. 2014), which are bounded by faults, and are from east to west: 1) the Tally Pond group; 2) the Long Lake group; 3) the Tulks group; 4) the Sutherlands Pond group; 5) the Pats Pond group; and 6) the Wigwam Pond group; the Tulks, Long Lake, and Tally Pond groups are known to host VMS deposits. These six tectonic assemblages yield U-Pb zircon ages ranging from ~513 to 453 Ma (Dunning *et al*. 1987; Evans *et al*. 1990; Dunning *et al*. 1991; Evans & Kean 2002; Zagorevski *et al*. 2007; McNicoll *et al*. 2010). Furthermore, the Tally Pond group is informally subdivided into the felsic volcanic rock dominated Bindons Pond formation (also referred to as Boundary Brook formation) and the mafic volcanic rock dominated Lake Ambrose formation (Rogers *et al*. 2006). The latter contains island arc tholeiitic basalts to andesites with εNd_{511} of +3.1 (Dunning *et al*. 1991; Evans & Kean 2002; Rogers *et al*. 2006), whereas the former contains predominantly transitional to calc-alkalic rhyolitic to dacitic rocks with εNd_{511} of +1.8 to +2.6 (Rogers *et al*. 2006; Piercey *et al*. 2014). The Cambrian felsic volcanic rocks of the Bindons Pond formation contain inherited zircons with Neoproterozoic U-Pb ages of 563 Ma (McNicoll *et al*. 2010).

Deposit Geology and Lithofacies

The Lemarchant VMS deposit is hosted within the Bindons Pond formation and is capped by a <1 to 20 m thick layer of metalliferous mudstones occurring at the contact between the Bindons Pond and Lake Ambrose formations (Fig. 3A; Copeland *et al*. 2009; Fraser *et al*. 2012; Lode *et al*. 2015). These sulphide-rich metalliferous mudstones extend discontinuously around the massive sulphides for one to four kilometres (Copeland *et al*. 2009; Fraser *et al*. 2012; Lode *et al*. 2015). Three main types of exhalative mudstones occur at the Lemarchant deposit: 1) mudstones immediately on top of massive sulphide mineralization between the felsic and mafic volcanic rocks (exhalative mudstone-massive sulphide (EMS)-type; Fig. 3A-C, G-H); 2) mudstones extending laterally outwards from mineralization, but at the same stratigraphical level and without immediate association with mineralization (felsic-exhalative mudstone-mafic (FEM)-type; Fig. 3D); or 3) interflow mudstones within the hanging wall basaltic rocks (interflow exhalative mudstone (IFE)-type; Fig. 3E). Interflow mudstones occur commonly within 15 meters above the massive sulphide mineralization, but are present up to 70 meters above the ore horizon. Independent of their stratigraphical positions, the mudstones are brown to black, graphite-rich, finely laminated, and contain fine carbonaceous/organic-rich laminae that are intercalated with siliciclastic, volcaniclastic and/or amorphous kidney-shaped chert±apatite layers (Fig. 3C, F). The main sulphide phases are pyrite (framboidal, massive and euhedral) and pyrrhotite, with minor marcasite, chalcopyrite, sphalerite, arsenopyrite and galena. Contents of chalcopyrite, sphalerite, and galena increase proximal to mineralization. The sulphides occur both parallel to bedding, and in later stage, stringer-like veins (Fig. 3A, D-E).

Methodology

Sampling, methods, and quality control and quality assurance (QA/QC)

Samples were collected during stratigraphical mapping and drill core logging of the Lemarchant deposit from drill holes that have metalliferous mudstones and include the Lemarchant Main Zone, the Northwest and 24 zones, as well as the North and South targets (Fig. 4A). Samples were taken from representative exhalative mudstone types (EMS, FEM, and IFE), tuff, and surrounding lithological mafic and felsic volcanic units. The whole rock lithogeochemical data were previously evaluated and presented in Lode *et al*. (2015), including analytical methods and QA/QC for lithogeochemical data. Lithogeochemical data are reproduced here only to compare to Nd isotope results.

Neodymium isotopes

Twelve representative samples of the Lemarchant mudstones were selected for Nd isotopic determinations from the three mudstone types and tuffs that are intercalated with the mudstones. These samples were chosen to cover both the horizontal and vertical distributions of all mudstones types and tuff occurring in the Lemarchant area. Additionally, one least altered sample of the felsic and mafic volcanic rocks (Fig. 3G-H) were selected for analyses, and for comparison to mudstone samples. Samarium and Nd isotopic compositions were measured at Memorial University using a multicollector Finnigan MAT 262 thermal ionization mass spectrometer (TIMS) in static and dynamic acquiring modes. Samples for Nd analyses were prepared using the methods of Fisher *et al*. (2011) from whole-rock powders using a multi-acid (HF, HNO_3, and HCl) dissolution-evaporation process following methods. Separation of Sm and Nd was obtained using conventional two-step column chemical methods (Fisher *et al*. 2011). Accuracy and precision for the Nd analyses were determined using the standards JNdi-1 and BCR-2 as reference materials following methods described in Fisher *et al*. (2011). The JNdi-1 and BCR-2 standards have following reported values: $^{143}Nd/^{144}Nd$ = 0.512115 and $^{143}Nd/^{144}Nd$ = 0.512633, respectively (Tanaka *et al*. 2000; Raczek *et al*. 2003). Standards were run every 11 samples with each analytical batch. Additionally, blanks were utilized during each analytical run to test contamination; none was detected. Precision was determined using the percent relative standard deviation (%RSD) on the replicate analyses of the reference materials, and accuracy was determined using percent relative difference (%RD) from accepted values. Analyses for the Lemarchant samples have an average 0.0013 %RSD for $^{143}Nd/^{144}Nd$ and 0.00055 %RD for $^{143}Nd/^{144}Nd$. The results herein are presented using the epsilon notation (εNd) and calculated for a formation age of 513 Ma, the U-Pb age of the host stratigraphy as reported by Dunning *et al*. (1991); data are presented in Table 1 and Figures 4B, 5A-B, and Figure 8. εNd_{513} was calculated by $\varepsilon Nd_t = (^{143}Nd/^{144}Nd_{rock,t} \,/\, ^{143}Nd/^{144}Nd_{CHUR,t}) \times 10^4$ after Rollinson (1993) and $f^{Sm/Nd} = [(^{147}Sm/^{144}Nd_{sample,t}) \,/\, (^{147}Sm/^{144}Nd_{CHUR,t}) - 1]$ after McLennan *et al*. (1990). Chondrite uniform reservoir (CHUR) values utilized in this study are $^{143}Nd/^{144}Nd$ of

0.512638 and a $^{147}Sm/^{144}Nd$ of 0.1967 (Hamilton *et al*. 1983; Rollinson 1993). Depleted mantel model ages (T_{DM}) were calculated using depleted mantle values of $^{144}Nd/^{144}Nd$ = 0.513163 and $^{147}Sm/^{144}Nd$ = 0.2137, and a decay constant of $\lambda = 6.54 \times 10^{-12}$ (DePaolo 1981).

Results

Neodymium isotopic systematics. The Lemarchant mudstones (n = 10), have εNd_{513} = –6.0 to −1.8 and T_{DM} = 1.63 to 3.05 Ga (Table 1). Overall, the three types of Lemarchant mudstones (EMS = proximal; FEM = distal; IFE = interflow) have similar εNd_{513} values; however, the EMS-type have slightly lower εNd_{513} values and range from –5.6 to –4.1 with an average of –4.8, the FEM-type are less evolved and range from εNd_{513} = –4.0 to −3.2 with an average of −3.7, and the IFE-type has the widest range of εNd_{513} = –6.0 to −1.8 and average of –3.9 (Table 1; Fig. 4B, 5A-B). The Lemarchant tuff samples (n = 2) have εNd_{513} = –5.7 to –4.7 with an average of –5.2 and T_{DM} = 1.75 to 1.81 Ga. In εNd versus Th/Sc space the Lemarchant mudstones and tuff have Th/Sc ratios of 0.06 to 1.93 and fall between the arc andesite fields, with samples that have greater Th/Sc containing lower εNd values like the upper crust (Fig. 5A). These more evolved samples also trend towards the field of the 563 Ma Crippleback Intrusive Suite and Sandy Brook Group crustal basement rocks (recalculated here at 513 Ma for comparison; Fig. 5A). The Lemarchant felsic and mafic volcanic rock measured in this study (one each) have εNd_{513} = +0.4 and a T_{DM} = 1.47 Ga, and εNd_{513} = +1.4 and a T_{DM} = 1.74 Ga, respectively, and plot in the field for arc rocks (Table 1; Fig. 5B). These values for the Lemarchant volcanic rocks are similar to values reported by Rogers *et al*. (2006) and McNicoll *et al*. (2010) for felsic and mafic volcanic rocks of the Tally Pond volcanic belt, including samples from the 'Upper Block' and the 'Mineralized Block' of the Duck Pond deposit (Fig. 5B).

The $f^{Sm/Nd}$ reflects the fractional deviation of $^{147}Sm/^{144}Nd$ from CHUR in parts per 10^4 because of light rare earth element enrichment (i.e., lower Sm/Nd) during igneous differentiation processes (McLennan *et al*. 2003). Accordingly, in $f^{Sm/Nd}$-εNd space (Fig. 5B) the Lemarchant mudstone and tuff samples have more evolved εNd_{513} values than the Lemarchant volcanic rocks, and are overall comparable in εNd to values reported by Rogers *et al*. (2006) for the Neoproterozoic Crippleback quartz monzonite and Sandy Brook Group rhyolite. However, the Lemarchant mudstone and tuff samples have $f^{Sm/Nd}$ higher than the Neoproterozoic Crippleback quartz-monzonite and Sandy Brook Group rhyolite and trend towards those of the Tally Pond group volcanic rocks (Fig. 5B; McLennan *et al*. 2003). The εNd values of the Lemarchant mudstone and tuff samples do not show any spatial variations throughout the zones of the deposit and/or with depth in the stratigraphy in the Lemarchant area (Fig. 4A-B). The T_{DM} = 1.63 to 3.05 Ga of the Lemarchant mudstones are older than reported values for the coeval felsic volcanic rocks of the 'Upper Block' and 'Mineralized Block' at Duck Pond of 1.06 and 1.35 Ga, and 0.95 Ga, respectively (McNicoll *et al*. 2010), and those of the Crippleback Intrusive Suite (1.26 and 1.35 Ga) and the Sandy Brook Group (1.15 to 1.34 Ga) (Rogers *et al*. 2006; this study).

Immobile element systematics: Volcanic rocks of the Tally Pond group that are associated with the hydrothermal sedimentary rocks and volcanic and igneous rocks of the Sandy Brook Group and Crippleback Intrusive Suites are shown on the immobile element Zr/Ti-Nb/Y classification diagram by Winchester and Floyd (1977) and Pearce

(1996) in Figure 6a. This diagram enables to discriminate and identify rock types, independently from the degree of alteration (Winchester & Floyd 1977; Pearce 1996). The volcanic rocks from the Lemarchant deposit are subalkaline basaltic andesites, with the more felsic rocks trending towards dacite boundary, and the more mafic rocks trending towards the basalt boundary (Fig. 6A). Because of the limited sample number for volcanic rocks from this study, fields from Cloutier *et al*. (*in press)* were added for felsic, intermediate, and mafic volcanic rocks from the Lemarchant deposit (Fig. 6A). Additionally, samples for Tally Pond belt felsic and mafic volcanic rocks, the Sandy Brook Group rhyolite and basalt and Crippleback quartz monzonite of Rogers (2004) and Rogers et al (2006) were also added for comparison. Chemically, the volcanic rocks of Lemarchant show a wide distribution, with felsic-dominated rhyolite-dacites of the Bindons Pond formation as well as intermediate andesite-basaltic andesites and mafic rocks of the Lake Ambrose formation (Cloutier *et al*. *in press*). The alteration-independent Nb-Y diagram after Pearce *et al*. (1984), which discriminates the general tectonic settings, shows that the Tally Pond belt volcanic rocks plot predominantly in the volcanic arc field (Fig. 6B), which is consistent with potential source rocks for the detrital constituent in the hydrothermal sedimentary rocks and regional models for the Tally Pond group (e.g., Rogers *et al*. 2007; Piercey *et al*. 2014).

Discussion

Provenance, tectonic setting, and the role of crustal input

The Tally Pond volcanic belt represents the oldest magmatism of the Penobscot Arc and was developed during phases of arc rifting at the leading edge of the Ganderian margin

(Rogers *et al*. 2006; Zagorevski *et al*. 2010; Piercey *et al*. 2014).

Penecontemporaneously, further rifting on the trailing edge of Ganderia, led to the formation of the Ellsworth belt (~509-505 Ma) of coastal Maine and New Brunswick representing the separation of Ganderia from the Gondwanan Amazonian margin (Fyffe *et al*. 2009; van Staal *et al*. 2012). The volcanic rocks of the Ellsworth terrane comprise tholeiitic basalts and rhyolites with $\varepsilon Nd_{500\ Ma}$ values ranging from +5.6 to +8.6, but also calc-alkaline rhyolite (R-1 Rhyolite) that yielded $\varepsilon Nd_{500\ Ma}$ values near zero (Schulz *et al*. 2008). The latter are similar to εNd values of felsic and mafic volcanic rock samples from the Tally Pond belt (Bindons Pond and Lake Ambrose formations) of this study (εNd = +1.4 and +0.4, respectively), which are comparable with values that were previously reported for the Tally Pond volcanic rocks (Fig. 5B; Rogers *et al*. 2006; Zagorevski *et al*. 2010). This illustrates that the Lake Ambrose formation basalts have predominantly juvenile signatures ($\varepsilon Nd_{511\ Ma}$ = +3; Rogers *et al*. 2006 and this study), whereas Bindons Pond formation rhyolites and dacites have less juvenile values (εNd_{511Ma} = +1.8 and +2.6) (Rogers *et al*. 2006; Zagorevski *et al*. 2010). There is a noticeable difference in $\varepsilon Nd_{513\ Ma}$ values between the sedimentary and volcanic rocks of the Lemarchant deposit, however. In general, the mudstones and tuffs have lower εNd_{513} values ranging from −6.0 to −1.8 (Fig. 5A-B), similar to the Sandy Brook Group rhyolite $\varepsilon Nd_{513\ Ma}$ = −6.5 to −1.9, as well as those of the Crippleback Intrusive Suite $\varepsilon Nd_{513\ Ma}$ = −5.9 to −5.2 (Rogers *et al*. 2006). Moreover, the Lemarchant mudstones have similar $\varepsilon Nd_{513\ Ma}$ values throughout the sections of the Lemarchant Main Zone, the Northwest and 24 zones, and the North Target (Fig. 4A-B), albeit proximal Lemarchant mudstones (EMS-type) have more evolved εNd_{513} values than the more distal mudstones (FEM-type; Figs. 4A-B).

There are a number of potential Nd sources in hydrothermal mudstones, including seawater-derived/scavenged, detrital, and hydrothermally-derived components (Goldstein *et al*. 1984; Mills *et al*. 1993; Mills & Elderfield 1995). Scavenging of REE from seawater occurs during mixing of the hydrothermal fluids with seawater, where oxyanions (HPO_4^{2-}, HVO_4^{2-}, CrO_4^{2-}, $HAsO_4^{2-}$), trace elements, and rare earth elements (REE, including Nd) are scavenged from seawater onto Fe-oxyhydroxides, and subsequently deposited on the mount flanks and in topographic depressions around the hydrothermal vent site in a rift-graben or caldera basin (de Baar *et al*. 1988; Rudnicki 1995; German & Von Damm 2003; Peter 2003). Nd isotopic signatures measured from modern seawater show a wide range that indicate that continental Nd is the predominant source of REE in modern seawater resulting in different Nd values within the main water masses/oceans (Goldstein *et al*. 1984; Bertram & Elderfield 1993; Tachikawa *et al*. 2003). Thus, exposure of crustal basement during arc rifting would bring crustal-derived evolved Nd into the ambient seawater, together with Nd derived from the continuously erupting and erosion of the more juvenile Cambrian Tally Pond volcanic rocks. The Nd is contributed to the Nd budget of hydrothermal sediment either dissolved or as detrital particles, and via adsorption onto hydrothermally-derived particles, such as Fe-oxyhydroxides (Wood & Williams-Jones 1994; Mills & Elderfield 1995; Rudnicki 1995; Chavagnac *et al*. 2005). In contrast, hydrothermal Nd is a minimal component in hydrothermal sediment, mostly because REE are in extremely low concentrations in seafloor hydrothermal fluids and initial hydrothermal Nd signatures in the hydrothermal sediment are often rapidly overprinted by Nd scavenged from seawater (Elderfield 1988; Mills *et al*. 1993; Mills & Elderfield 1995). Most hydrothermal sediment contains up to

~80% hydrothermally-derived matter (i.e., derived directly from the fluid and scavenged from seawater), whereas the remainder consists of sedimentary detritus, including volcaniclastic and epiclastic material and windblown dust, which are also possible Nd sources in metalliferous sediments (Boström *et al*. 1972; Boström 1973; Cavanagh *et al*. 2005; Goldstein *et al*. 1984).

Considering these processes and potential Nd sources, it is noticeable that even though the Lemarchant hydrothermal sediments predominantly consist of hydrothermally-derived matter (e.g., Zn-Pb-Cu-Fe-S), their Nd budget contains only minor hydrothermally-derived Nd. The dilution of hydrothermal fluids by seawater, scavenging processes, and contributions of detrital matter generally annihilates the initial hydrothermal Nd signatures in hydrothermal sediments (Mills & Elderfield 1995).

Because of the restricted nature of a rifted arc basin, where predominantly locally occurring provenance rocks (i.e., Tally Pond volcanic rocks, Crippleback Intrusive Suite and Sandy Brook Group basement rocks) are eroded, this locally-derived detrital Nd is subsequently archived in the hydrothermal sedimentary rocks within the basin (Figs. 7A-B, 8). The Nd in these hydrothermal sediments was derived predominantly from scavenging and detrital matter, which explains their evolved Nd signatures; signatures that are not present in the more juvenile Tally Pond volcanic rocks. Furthermore, it is suggested that the more evolved Nd signatures of the proximal mudstones represent early stages of arc-rifting, which were dominated by erosion of the rifted Neoproterozoic Ganderian and possibly older crustal basement, whereas the more distal mudstones reflect greater contributions from the continuously erupting and erosion of the more juvenile Cambrian Tally Pond group volcanic rocks (Fig. 7A-B).

The presence of Neoproterozoic Ganderian arc rocks (Crippleback Intrusive Suite and coeval Sandy Brook Group) beneath the Tally Pond volcanic belt is indicated by inherited zircons (563 Ma) in the Cambrian felsic volcanic rocks of the Tally Pond belt (Rogers *et al*. 2006; Rogers *et al*. 2007; McNicoll *et al*. 2010; Zagorevski *et al*. 2010). Neoproterozoic (~553 Ma) inherited zircon ages are also known from the Pats Pond group (~487 Ma), which also have Mesoproterozoic (0.9-1.2 Ga) xenocrystic zircons (Zagorevski *et al*. 2007, Zagorevski *et al*. 2010). Plutonic and gneissic boulders, as well as sedimentary rocks from the Ellsworth Formation of coastal Maine and New Brunswick contained small populations of Mesoproterozoic, Palaeoproterozoic, and Archean zircons up to 3.23 Ga, but with a dominant population between 1.07 to 1.61 Ga (Hibbard *et al*. 2007; Schulz *et al*. 2008; Fyffe *et al*. 2009; van Staal *et al*. 2012). These inherited zircon patterns are consistent for a location of Ganderia along the Gondwanan Amazonian margin (Fyffe *et al*. 2009; van Staal *et al*. 2012). The Mesoproterozoic to Archean T_{DM} model ages and Nd isotopic data of the Lemarchant mudstones (1.63 to 3.05 Ga) together with the detrital zircon populations and the Nd signatures of the Tally Pond volcanic rocks, as well as of the Crippleback Intrusive Suite and Sandy Brook Group, indicate an Amazonian provenance, which suggests that the Tally Pond belt also evolved along this margin (Fig. 8; Zagorevski *et al*. 2007; Pollock *et al*. 2011; van Staal & Barr 2011; van Staal *et al*. 2012).

Significant input from crustal material is further supported by the Pb isotopic data of the Lemarchant deposit and other massive sulphide occurrences in the Tally Pond belt (Swinden & Thorpe 1984; Pollock & Wilton 2001; Gill 2015; Lode *et al*. 2017). Volcanogenic massive sulphides and associated hydrothermal sediments have Pb sources that derive their Pb predominantly from leaching of basement rocks, which may include different reservoirs (Franklin *et al*. 1981; Swinden & Thorpe 1984; Tosdal *et al*. 1999; Ayuso *et al*. 2003). Lead isotopic data measured *in-situ* on galena hosted within sulphides in the hydrothermal sediments using secondary ion mass spectrometry (SIMS), suggested hydrothermally- and detritally-derived Pb sources (Lode *et al*. 2017). Especially more vent distal mudstones showed more radiogenic detritally Pb contributions, which were characterised by more radiogenic $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios (Mills & Elderfield 1995; Lode *et al*. 2017).

Altogether, the Nd and Pb isotopic data support that older crustal basement plays a role in hydrothermal activity, either through direct leaching (Pb), detrital (Pb+Nd), or via adsorption/deposition from the water column (Nd). Furthermore, trace element signatures of the Tally Pond volcanic rocks and provenance-related immobile element systematics of the metalliferous mudstones are consistent with a formation in a volcanic arc environment, such as a graben/caldera in a rifted continental arc, or an arc proximal to continental crust (Rogers *et al*. 2006; Zagorevski *et al*. 2010; Piercey *et al*. 2014). Therefore, the metalliferous mudstones that precipitate in a rifted arc basin/caldera setting record the provenance components of the lithologies present in the basin and may be useful for palaeogeographic reconstructions and additionally provide means to determine the source of metals that contributed to the formation of the genetically associated massive sulphides.

Conclusions

It is proposed that the volcanogenic massive sulphides of the Lemarchant deposit and related exhalative metalliferous mudstones that are associated with felsic, intermediate, and mafic volcanic rocks are formed from fluids that ascend along deep synvolcanic faults in a rifted arc basin. Eruption and erosion of the Tally Pond belt volcanic rocks that were formed in this rift-related graben/caldera setting, added juvenile Nd to the system. The hydrothermal sediments precipitate in an environment, where Ganderian arc rocks of the Crippleback Intrusive Suite and the coeval Sandy Brook Group was exposed and eroded, which contributed evolved crustal Nd to the ambient seawater. Based on detrital zircon and Nd isotopic studies it is further suggested that unexposed older crustal basement of the Gondwanan Amazonian margin beneath the Ganderian arc rocks additionally contributed evolved Nd to the Nd budget in the metalliferous mudstones. The precipitating hydrothermal metalliferous mudstones record the mixed, i.e., evolved and juvenile, εNd signatures. Furthermore, the hydrothermal sediments have more evolved εNd systematics than the spatially associated Tally Pond belt volcanic rocks indicating the presence of eroded older crustal material that did not significantly contribute to the volcanic rocks. Overall, the Nd isotopic compositions, as well as the lithogeochemical data, of the Lemarchant metalliferous mudstones and suggests that the Lemarchant deposit hydrothermal mudstones record formation within a rifted arc environment built upon Ganderian (exposed) and Gondwanan Amazonian (unexposed) crustal basement, consistent with existing models for the Tally Pond group.

Acknowledgements

Kind support was provided by Dianne and Charlie Fost, Michael Vande Guchte, Alexandria Marcotte, and Gerry Squires from Paragon Minerals Corporation (a 100%-

owned subsidiary of Canadian Zinc Corporation). The authors would further like to thank Keir Hiscock, Pam King, Sherry Strong, Anne Westhues, as well as Luke Beranek and Greg Dunning for the helpful reviews and Inês Nobre Silva for general discussions, help, and support.

Funding information

Research funded by the Canadian Mining Research Organization (CAMIRO, Project 08E04) and grants of the Natural Sciences and Engineering Research Council of Canada (NSERC): NSERC Discovery Grant – 249695-2011; NSERC IRC Grant – 408433-09; NSERC CRD Grant – CAMIRO Project – CRDPJ 387592-09; RDC and a grant of the Research and Development Corporation of Newfoundland and Labrador (RDC) RDC IRIF for IRC – 5003.121.001 to Dr. Stephen Piercey. Research was also funded by the NSERC-Altius Industrial Research Chair in Mineral Deposits, funded by NSERC, Altius Resources Inc.

References

Ayuso, R.A. & Schulz, K.J. 2003. Nd-Pb-Sr isotope geochemistry and origin of the Ordovician Bald Mountain and Mount Chase massive sulfide deposits, northern Maine. *Economic Geology Monographs*, **11**, 611-630.

Bertram, C.J. & Elderfield, H. 1993. The geochemical balance of the rare earth elements and neodymium isotopes in the oceans. *Geochimica et Cosmochimica Acta*, **57**, 1957-1986.

Chavagnac, V., German, C.R., Milton, J.A. & Palmer, M.R. 2005. Sources of REE in sediment cores from the Rainbow vent site (36°14′N, MAR). *Chemical Geology*, **216**, 329-352, doi: 10.1016/j.chemgeo.2004.11.015.

Cloutier, J., Piercey, S.J., Lode, S., Vande Guchte, M. & Copeland, D.A. in press. Lithostratigraphic and structural reconstruction of the Zn-Pb-Cu-Ag-Au Lemarchant volcanogenic massive sulphide (VMS) deposit, Tally Pond group, central Newfoundland, Canada. *Ore Geology Reviews*. http://dx.doi.org/10.1016/j.oregeorev.2017.01.010

Copeland, D.A., Toole, R.M. & Piercey, S.J. 2009. 10th Year Supplementary Assessment Report on Soil Sampling, Linecutting, Titan 24 Geophysical Surveying, Diamond Drilling and Petrography, Licence 8183M, South Tally Pond Property, Rogerson Lake Area, Newfoundland and Labrador, NTS 12A/10 and 12A/07. *Newfoundland and Labrador Geological Survey Assessment File*.

de Baar, H.J.W., German, C.R., Elderfield, H. & van Gaans, P. 1988. Rare earth element distributions in anoxic waters of the Cariaco Trench. *Geochimica et Cosmochimica Acta*, **52**, 1203-1219.

DePaolo, D.J. 1981. Neodymium isotopes in the Colorado Front Ranges and crust-mantle evolution in the Proterozoic. *Nature*, **291**, 193-196, doi: doi:10.1038/291193a0.

Dunning, G.R., Kean, B.F., Thurlow, J.G. & Swinden, H.S. 1987. Geochronology of the Buchans, Roberts Arm, and Victoria Lake groups and Mansfield Cove Complex, Newfoundland. *Canadian Journal of Earth Sciences,* **24**, 1175-1184.

Dunning, G.R., Swinden, H.S., Kean, B.F., Evans, D.T.W. & Jenner, G.A. 1991. A Cambrian island arc in Iapetus; geochronology and geochemistry of the Lake Ambrose volcanic belt, Newfoundland Appalachians. *Geological Magazine*, **128**, 1-17.

Elderfield, H., Charnock, H., Lovelock, J.E., Liss, P.S. & Whitfield, M. 1988. The oceanic chemistry of the rare-earth elements. *Philosophical Transactions of the Royal Society of London, Series A: Mathematical and Physical Sciences*, **325**, 105-124.

Evans, D.T.W. & Kean, B.F. 2002. The Victoria Lake Supergroup, central Newfoundland - its definition, setting and volcanogenic massive sulphide mineralization. *Newfoundland and Labroador Department of Mines and Energy, Geological Survey, Open File NFLD/2790*.

Fisher, C.M., McFarlane, C.R.M., Hanchar, J.M., Schmitz, M.D., Sylvester, P.J., Lam, R. & Longerich, H.P. 2011. Sm-Nd isotope systematics by laser ablation-multicollector-inductively coupled plasma mass spectrometry: Methods and potential natural and synthetic reference materials. *Chemical Geology*, **284**, 1-20.

Franklin, J.M., Sangster, D.M. & Lydon, J.W. 1981. Volcanic-associated massive sulfide deposits. *In*: Skinner, B.J. (ed.) *Economic Geology Seventy-Fifth Anniversary Volume*. Society of Economic Geologists, 485-627.

Fraser, D., Giroux, G.A., Copeland, D.A. & Devine, C.A. 2012. *NI-43-101* Technical Report and Mineral Resource Estimate on the Lemarchant Deposit, South Tally Pond VMS Project, central Newfoundland, Canada for Paragon Minerals Corporation. *National Instrument 43-101 Technical Report*.

Fyffe, L.R., Barr, S.M., Johnson, S.C., McLeod, M.J., McNicoll, V.J., Valverde-Vaquero, P., van Staal, C.R. & White, C.E. 2009. Detrital zircon ages from Neoproterozoic and Early Proterozoic conglomerate and sandstone units of New Brunswick and coastal Maine: implications for the tectonic evolution of Ganderia. *Atlantic Geology*, **45**, 110-144.

Gale, A., Langmuir, C.H. & Dalton, C.A. 2014. The global systematics of Ocean Ridge Basalts and their origin. *Journal of Petrology*, **55**, 1051-1082.

Galley, A.G., Hannington, M. & Jonasson, I. 2007. Volcanogenic massive sulphide deposits. *In*: Goodfellow, W.D. (ed.) *Mineral Deposits of Canada: A Synthesis of Major Deposit-types, District Metallogeny, the Evolution of Geological Provinces, and*

Exploration Methods. Special Publication 5, Mineral Deposits Division, Geological Association of Canada, 141-161.

German, C.R. & Von Damm, K.L. 2003. Hydrothermal Processes. *Treatise on Geochemistry*. Pergamon, Oxford, 181-222.

Gibson, H.L., Allen, R.L., Riverin, G. & Lane, T.E. 2007. The VMS model: Advances and application to exploration targeting. *In*: Milkereit, B. (ed.) *Proceedings of Exploration 07: Fifth Decennial International Conference on Mineral Exploration*, Toronto, ON, 717-730.

Gill, S.B. 2015. Mineralogy, metal zoning, and genesis of the Zn-Pb-Ba-Ag-Au Lemarchant volcanogenic massive sulfide (VMS) deposit. *M.Sc. Thesis*, Memorial University of Newfoundland.

Goldstein, S.L., O'Nions, R.K. & Hamilton, P.J. 1984. A Sm-Nd isotopic study of atmospheric dusts and particulates from major river systems. *Earth and Planetary Science Letters*, **70**, 221-237.

Grenne, T. & Slack, J.F. 2003. Bedded jaspers of the Ordovician Lokken Ophiolite, Norway; seafloor deposition and diagenetic maturation of hydrothermal plume-derived silica-iron gels. *Mineralium Deposita*, **38**, 625-639.

Hamilton, P.J., O'Nions, R.K., Bridgwater, D. & Nutman, A. 1983. Sm-Nd studies of Archaean metasediments and metavolcanics from West Greenland and their implications for the Earth's early history. *Earth and Planetary Science Letters*, **63**, 263-273.

Hannington, M.D., de Ronde, C.E.J. & Petersen, S. 2005. Sea floor tectonics and submarine hydrothermal systems. *In*: Hedenquist, J.W., Thompson, J.F.H., Goldfarb, R.J. & Richards, J.P. (eds.) *Economic Geology: One Hundredth Anniversary Volume, 1905-2005*. Society of Economic Geologists, Littleton, CO, USA, 111-142.

Hannington, M.D., Jonasson, I.R., Herzig, P.M. & Petersen, S. 1995. Physical and chemical processes of seafloor mineralization at mid-ocean ridges. *Geophysical Monograph*, **91**, 115-157.

Hekinian, R., Hoffert, M., Larqué, P., Cheminée, J.L., Stoffers, P. & Bideau, D. 1993. Hydrothermal Fe and Si oxyhydroxide deposits from South Pacific intraplate volcanoes and East Pacific Rise axial and off-axial regions. *Economic Geology*, **88**, 2099-2121.

Hibbard, J.P., van Staal, C.R. & Rankin, D.W. 2007. A comparative analysis of pre-Silurian crustal building blocks of the northern and the southern Appalachian orogen. *American Journal of Science*, **307**, 23-45, doi: 10.2475/01.2007.02.

Hollis, S.P., Cooper, M.R., Herrington, R.J., Roberts, S., Earls, G., Verbeeten, A., Piercey, S.J. & Archibald, S.M. 2015. Distribution, mineralogy and geochemistry of silica-iron exhalites and related rocks from the Tyrone Igneous Complex: Implications for VMS mineralization in Northern Ireland. *Journal of Geochemical Exploration*, **159**, 148-168, doi: http://dx.doi.org/10.1016/j.gexplo.2015.09.001.

Huston, D., Relvas, J., Gemmell, J. & Drieberg, S. 2011. The role of granites in volcanic-hosted massive sulphide ore-forming systems: an assessment of magmatic–hydrothermal contributions. *Mineralium Deposita*, **46**, 473-507, doi: 10.1007/s00126-010-0322-7.

Huston, D.L., Pehrsson, S., Eglington, B.M. & Zaw, K. 2010. The geology and metallogeny of volcanic-hosted massive sulfide deposits: Variations through geologic time and with tectonic setting. *Economic Geology*, **105**, 571-591, doi: 10.2113/gsecongeo.105.3.571.

Ickert, R.B. 2013. Algorithms for estimating uncertainties in initial radiogenic isotope ratios and model ages. *Chemical Geology*, **340**, 131-138, doi: 10.1016/j.chemgeo.2013.01.001.

Jenner, G.A. & Swinden, H.S. 1993. The Pipestone Pond Complex, central Newfoundland; complex magmatism in an eastern Dunnage Zone ophiolite. *Canadian Journal of Earth Sciences*, **30**, 434-448.

Keto, L.S. & Jacobson, S.B. 1988. Nd isotopic variations of Phanerozoic palaeoceans. *Earth and Planetary Science Letters*, **90**, 395-410.

Lode, S., Piercey, J.S. & Devine, C.A. 2015. Geology, mineralogy, and lithogeochemistry of metalliferous mudstones associated with the Lemarchant volcanogenic massive sulfide deposit, Tally Pond belt, central Newfoundland. *Economic Geology*, **110**, 1835-1859.

Lode, S., Piercey, S.J., Layne, G.D., Piercey, G. & Cloutier, J. 2017. Multiple sulphur and lead sources recorded in hydrothermal exhalites associated with the Lemarchant volcanogenic massive sulphide deposit, central Newfoundland, Canada. *Mineralium Deposita*, **52**, 105-128, doi: 10.1007/s00126-016-0652-1.

Lydon, J.W. 1984. Ore deposit models; 8, Volcanogenic sulphide deposits; Part I, A descriptive model. *Geoscience Canada*, **11**, 195-202.

McCulloch, M.T. & Wasserburg, G.J. 1978. Sm-Nd and Rb-Sr chronology of continental crust formation. *Science*, **200**, 1003-1011.

McLennan, S.M., Bock, B., Hemming, S.R., Hurowitz, J.A., Lev, S.M. & McDaniel, D.K. 2003. The roles of provenance and sedimentary processes in the geochemistry of sedimentary rocks. *In*: Lentz, D.R. (ed.) *Geochemistry of Sediments and Sedimentary Rocks: Evolutionary Considerations to Mineral Deposit-Forming Environments*. Geological Association of Canada, St. John's, NL, Canada, 7-38.

McLennan, S.M., Hemming, S., McDaniel, D.K. & Hanson, G.N. 1993. Geochemical approaches to sedimentation, provenance, and tectonics. *Special Paper Geological Society of America*, **284**, 21-40.

McLennan, S.M., Taylor, S.R., McCulloch, M.T. & Maynard, J.B. 1990. Geochemical and Nd-Sr isotopic composition of deep-sea turbidites; crustal evolution and plate tectonic associations. *Geochimica et Cosmochimica Acta*, **54**, 2015-2050.

McNicoll, V., Squires, G., Kerr, A. & Moore, P. 2010. The Duck Pond and Boundary Cu-Zn deposits, Newfoundland: new insights into the ages of host rocks and the timing of VHMS mineralization. *Canadian Journal of Earth Sciences*, **47**, 1481-1506.

Mills, R., Elderfield, H. & Thomson, A. 1993. A dual origin for the hydrothermal component in a metalliferous sediment core from the Mid-Atlantic Ridge. *Journal of Geophysical Research*, **98**, 9671-9681.

Mills, R.A. & Elderfield, H. 1995. Hydrothermal activity and the geochemistry of metalliferous sediment. *Geophysical Monograph*, **91**, 392-407.

Murphy, B.J., Waldron, J.W.F., Schofield, D.I., Barry, T.L. & Band, A. 2014. Highly depleted isotopic compositions evident in Iapetus and Rheic Ocean basalts: implications for crustal generation and preservation. *International Journal of Earth Sciences*, **103**, 1219-1232.

Nance, R.D., Murphy, J.B., Strachan, R.A., Keppie, J.D., Gutiérrez-Alonso, G., Fernández-Suárez, J., Quesada, C., Linnemann, U., D'Lemos, R. & Pisarevsky, S.A. 2008. Neoproterozoic - early Palaeozoic tectonostratigraphy and palaeogeography of the peri-Gondwanan terranes: Amazonian v. West African connections. *Geological Society of London*, **297**, 345-383.

Pearce, J.A. 1996. A user's guide to basalt discrimination diagrams. *In*: Wyman, D.A. (ed.) *Trace element geochemistry of volcanic rocks: Applications for massive sulphide exploration*. Geological Association of Canada, 79-113.

Peter, J.M. 2003. Ancient iron formations: their genesis and use in the exploration for stratiform base metal sulphide deposits, with examples from the Bathurst Mining Camp. *In*: Lentz, D.R. (ed.) *Geochemistry of Sediments and Sedimentary Rocks: Secular Evolutionary Considerations to Mineral Deposit-Forming Environments*. Geological Association of Canada, 145-176.

Piercey, S.J. 2007. Volcanogenic massive sulphide (VMS) deposits of the Newfoundland Appalachians: An overview of their setting, classification, grade-tonnage data, and unresolved questions. *In*: Pereira, C.P.G. & Walsh, D.G. (eds.) *Current Research*. Geological Survey Branch, St. John's, NL, 169-178.

Piercey, S.J., Squires, G.C. & Brace, T.D. 2014. Lithostratigraphic, hydrothermal, and tectonic setting of the Boundary volcanogenic massive sulfide deposit, Newfoundland Appalachians, Canada: Formation by subseafloor replacement in a Cambrian rifted arc. *Economic Geology*, **109**, 661-687, doi: 10.2113/econgeo.109.3.661.

Pollock, J.C. & Wilton, D.H.C. 2001. Metallogenic studies of the Tally Pond belt, Victoria Lake Group; trace-element geochemistry and lead-isotope data from the Exploits Subzone, Newfoundland. *Report - Government of Newfoundland and Labrador. Dept. of Mines and Energy, Geological Survey, Report: 2001-1, pp.247-266*.

Pollock, J.C., Wilton, D.H.C. & van Staal, C.R. 2002. Geological studies and definition of the Tally Pond Group, Victoria Lake Supergroup, Exploits Subzone, Newfoundland Appalachians. *Current Research - Newfoundland. Geological Survey Branch, Report: 02-1, pp.155-167*.

Pollock, J.C., Hibbard, J.P. & van Staal, C.R. 2011. A paleogeographical review of the peri-Gondwanan realm of the Appalachian orogeny. This article is one of a series of papers published in this CJES Special Issue: In honour of Ward Neale on the theme of Appalachian and Grenvillian geology. *Canadian Journal of Earth Sciences*, 259-288, doi: 10.1139/e11-049.

Raczek, I., Jochum, K.P. & Hofmann, A.W. 2003. Neodymium and strontium isotope data for USGS reference materials BCR-1, BCR-2, BHVO-1, BHVO-2, AGV-1, AGV-2, GSP-1, GSP-2 and eight MPI-DING reference glasses. *The Journal of Geostandards and Geoanalysis*, **27**, 173-179.

Rogers, N. 2004. Geochemical database, Red Indian Line project, central Newfoundland. *In*: Canada, G.S.o. (ed.), Open File 4605.

Rogers, N., van Staal, C.R., McNicoll, V., Pollock, J., Zagorevski, A. & Whalen, J. 2006. Neoproterozoic and Cambrian arc magmatism along the eastern margin of the Victoria Lake Supergroup: A remnant of Ganderian basement in central Newfoundland? *Precambrian Research*, **147**, 320-341.

Rogers, N., van Staal, C., Zagorevski, A., Skulski, T., Piercey, S.J. & McNicoll, V. 2007. Timing and tectonic setting of volcanogenic massive sulphide bearing terranes within the Central Mobile Belt of the Canadian Appalachians. *In*: Milkereit, B. (ed.) *Proceedings of Exploration 07: Fifth Decennial International Conference on Mineral Exploration*, Toronto, ON, 1199-1205.

Rollinson, H.R. 1993. Using geochemical data: evaluation, presentation, interpretation. Longman, 352 p.

Rudnicki, M.D. 1995. Particle formation, fallout and cycling within the buoyant and non-buoyant plume above the TAG vent field. *Geological Society, London, Special Publication*, **87**, 387-396, doi: 10.1144/gsl.sp.1995.087.01.30.

Schulz, K.J., Stewart, D.B., Tucker, R.D., Pollock, J.C. & Ayuso, R.A. 2008. The Ellsworth terrane, coastal Maine: Geochronology, geochemistry, and Nd-Pb isotopic composition--Implications for the rifting of Ganderia. *Geological Society of America Bulletin*, **120**, 1134-1158, doi: 10.1130/b26336.1.

Squires, G.C. & Hinchey, J.G. 2006. *Geology of the Tally Pond Volcanic Belt and Adjacent Areas (parts of NTS 12A/09 & 12A/10)*. *Map 2006-01*.

Squires, G.C. & Moore, P.J. 2004. Volcanogenic massive sulphide environments of the Tally Pond Volcanics and adjacent area; geological, lithogeochemical and geochronological results. *In*: Pereira, C.P.G., Walsh, D.G. & Kean, B.F. (eds.) *Current Research*. Geological Survey Branch, St. John's, NL, 63-91.

Swinden, H.S. 1988. Introduction to volcanogenic sulphide deposits in Newfoundland. *In*: Swinden, H.S. & Kean, B.F. (eds.) *The volcanogenic sulphide districts of central Newfoundland*. Geological Association of Canada, 1-26.

_____1991. Paleotectonic settings of volcanogenic massive sulphide deposits in the Dunnage Zone, Newfoundland Appalachians. *Canadian Institute of Mining and Metallurgy Bulletin*, **84**, 59-89.

Swinden, H.S. & Thorpe, R.I. 1984. Variations in style of volcanism and massive sulfide deposition in Early to Middle Ordovician island-arc sequences of the Newfoundland Central Mobile Belt. *Economic Geology*, **79**, 1596-1619.

Tachikawa, K., Athias, V. & Jeandel, C. 2003. Nedymium budget in the modern ocean and paleo-oceanographic implications. *Journal of Geophysical Research*, **108(C8)**, 3254.

Tanaka, T., Togashi, S., Kamioka, H., Amakawa, H., Kagami, H., Hamamoto, T., Yuhara, M., Orihashi, Y., Shigekazu, Y., Shimuzu, H., Kunimaru, T., Takahashi, K., Yanagi, T., Nakano, T., Fujimaki, H., Shinjo, R., Asahara, Y., Tanimizu, M. & Dragusanu, C. 2000. JNdi-1: a neodymium isotopic reference in consistency with LaJolla neodymium. *Chemical Geology*, **168**, 279-281.

Tivey, M.K. 2007. Generation of seafloor hydrothermal vent fluids and associated mineral deposits *Oceanography*, **20**, 50-65.

Tosdal, R.M., Wooden, J.L. & Bouse, R.M. 1999. Pb isotopes, ore deposits, and metallogenic terranes. *Reviews in Economic Geology*, **12**, 1-28.

van Staal, C.R. & Barr, S.M. 2011. Lithospheric architecture and tectonic evolution of the Canadian Appalachians and associated Atlantic margin. *In*: Percival, J.A., Cook, F.A. & Clowes, R.M. (eds.) *Chapter 2 Tectonic Styles in Canada: the LITHOPROBE Perspective*. Geological Association of Canada, 3-55.

van Staal, C.R., Barr, S.M. & Murphy, J.B. 2012. Provenance and tectonic evolution of Ganderia: Constraints on the evolution of the Iapetus and Rheic oceans. *Geology*, **40**, 987-990, doi: 10.1130/g33302.1.

Von Damm, K.L. 1990. Seafloor hydrothermal activity; black smoker chemistry and chimneys. *Annual Review of Earth and Planetary Sciences*, **18**, 173-204.

Williams, H. 1979. Appalachian Orogen in Canada. *Canadian Journal of Earth Sciences*, **16**, 792-807.

Williams, H., Colman-Sadd, S.P. & Swinden, H.S. 1988. Tectonostratigraphic subdivisions of central Newfoundland. *Current Research, Part B*. Geological Survey of Canada, Ottawa, ON, Canada, 91-98.

Winchester, J.A. & Floyd, P.A. 1977. Geochemical discrimination of different magma series and their differentiation products using immobile elements. *Chemical Geology*, **20**, 325-343.

Wood, S.A. & Williams-Jones, A.E. 1994. The aqueous geochemistry of rare-earth elements and yttrium. Part 4. Monazite solubility and REE mobility in exhalative massive sulfide-depositing environments. *Chemical Geology*, **115**, 135-162.

Zagorevski, A., van Staal, C.R., McNicoll, V.J. & Rogers, N. 2007. Upper Cambrian to Upper Ordovician peri-Gondwanan island arc activity in the Victoria Lake Supergroup, central Newfoundland; tectonic development of the northern Ganderian margin. *American Journal of Science*, **307**, 339-370.

Zagorevski, A., van Staal, C.R., Rogers, N., McNicoll, V.J. & Pollock, J. 2010. Middle Cambrian to Ordovician arc-backarc development on the leading edge of Ganderia, Newfoundland Appalachians. *Geological Society of America Memoir*, **206**, 367-396, doi: 10.1130/2010.1206(16).

Figure Captions

Fig. 1. (**a**) Tectonostratigraphical assemblages with the main zones of the Newfoundland Appalachians (Avalon, Gander, Dunnage, and Humber zones) and VMS occurrences within the Notre Dame and Exploits subzones.

Notre Dame Subzone VMS: 1 – York Harbour; 2 – 8 - Baie Verte Belt Deposits; 9 – 12, 46 – Springdale Belt Deposits; 13 – 29 Buchans-Roberts Arm Deposits.

Exploits Subzone VMS: 30 – 37 - Tulks Belt Deposits; Tally Pond Belt Deposits: 39 – Lemarchant; 40 – Duck Pond; 41 – Boundary; 42 – 45 – Point Leamington Belt Deposits. Modified after (Swinden, 1991) and Piercey (2007). (**b**) Geological map of the Tally Pond volcanic belt. The Tally Pond group comprises the Lemarchant deposit and the Duck Pond and Boundary mines. Figure after Copeland (2009) and Map 2006-01 from Squires and Hinchey (2006) and Lode et al. (2017).

Fig. 2. Schematic illustration of the main aspects of hydrothermal circulation in extensional tectonic environments. In the recharge zone seawater is entrained through crustal and progressively heated during downward migration. Water-rock interactions lead to loss of Mg^{2+}, SO_4^{2-}, and OH^- and H_2S is generated. These reactions produce H^+ and create acidic fluids that leach metals out of rocks. In the reaction zone the highest temperatures are reached and the hydrothermal fluids gain their geochemical signatures. The hot fluids rise buoyantly up along synvolcanic faults and are expelled vie hydrothermal plume into the ambient seawater. Figure modified after German and Von Damm (2003) and Gibson et al. (2007).

Fig. 3. Core photographs of the main Lemarchant mudstone types, tuff, and associated felsic and mafic volcanic rocks of the Bindons Pond and Lake Ambrose formations, respectively. (**a**) Finely laminated sulphide-rich EMS-type metalliferous mudstone with cross-cutting stringer type veins and overlying massive sulphide mineralization. Section 101N, LM11-65, mudstone sample CNF30983, 160.7 m. (**b**) Proximal EMS-type metalliferous mudstone associated with the Lemarchant Main Zone. Section 102+50N, LM10-43, CNF20976, 202.3 m. (**c**) Proximal EMS-type metalliferous mudstone with intercalated chert-apatite layers. Section 101N, LM07-13, CNF30954, 164.7 m. (**d**) FEM-type mudstone associated with the Northwest Zone. Section 106N, LM08-28, CNF20986, 240.6 m. (**e**) Sulphide-rich exhalative interflow mudstone. Section 101+25N, LM13-79, CNF25072, 169.0 m. (**f**) Lithic crystal vitric tuff that is intercalated with FEM-type mudstone. Section 100+50N, LM13-77, CNF25065, 140.0 m. (**g**) Felsic to intermediate volcanic rock of the Bindons Pond formation located in the North target. Section 108N, LM11-49, 144.6 m. (**h**) Mafic to intermediate volcanic rock of the Lake Ambrose formation located in the North target. Section 108N, LM11-49, 422.9 m.

Fig. 4. (**a**) Spatial distribution of εNd for the EMS-, FEM-, and IFE-type mudstones and tuff, as well as the Lemarchant felsic and mafic volcanic rock from this study. Sample data do not show any spatial variations throughout the sections and/or with depth in the stratigraphy in the Lemarchant area. 2σ error bars calculated after algorithm from Ickert (2013). (**b**) Resource map of the massive sulphides of the Lemarchant Main, 24 Zone, and Northwest Zone. Massive sulphides are projected to the surface. Modified from the resource map of Canadian Zinc Corporation.

Fig. 5. (**a**) Diagram of εNd versus Th/Sc ratio for the three main types of Lemarchant mudstones (EMS, FEM, and IFE) and tuff. Also plotted are data from Rogers *et al*. (2006) for felsic and mafic volcanic rocks of the Tally Pond belt and the Crippleback/Sandy Brook Group crustal basement rocks. Mid Ocean Ridge Basalt (MORB) field from data from Gale *et al*. (2014). Arc andesite field from data from Hawkeswoth *et al*. (1979). All data re-calculated for εNd_{513}. Diagram modified after McLennan *et al*. (1993). (**b**) Plot of $f^{Sm/Nd}$ versus εNd for the EMS-, FEM-, and IFE-type mudstones and tuff, as well as the Lemarchant felsic and mafic volcanic rock from this study. Also plotted are data from Rogers (2004) and Rogers *et al*. (2006) for felsic and mafic volcanic rocks of the Tally Pond belt, a felsic volcanic rock samples from the unmineralized Upper Block at Duck Pond and a sample from the Mineralized Block at Duck Pond from data from McNicoll *et al*. (2010), and the Crippleback/Sandy Brook Group crustal basement rocks. Diagram modified after McLennan *et al*. (1993).

Fig. 6. (**a**) and (**b**) Zr/Ti versus Nb/Y and Nb versus Y discrimination diagrams for volcanic rocks after Winchester and Floyd (1977) and Pearce (1996) for the Lemarchant felsic and mafic volcanic rocks from this study and from data from Rogers (2004) and Rogers *et al*. (2006). Additionally, data fields for felsic, intermediate, and mafic volcanic rocks was added (Cloutier, in press). Data from Rogers (2004) and Rogers *et al*. (2006) was also used to plot the Crippleback Lake/Sandy Brook Group crustal basement rocks.

Fig. 7. Model displaying the Cambrian Tally Pond belt with juvenile Nd signatures that is built upon the Ganderian and Gondwanan Amazonian rifted crustal basement with evolved Nd signatures. (**a**) Early stages of arc rifting with felsic volcanism and formation of massive sulphides and genetically associated metalliferous mudstones. Scavenged and detrital juvenile and evolved Nd is archived in archiving in the metalliferous mudstones resulting in mixed signatures. (**b**) Final stages of arc rifting and emplacement of mafic volcanic rocks that form the hanging wall to the Lemarchant VMS deposit.

Fig. 8. Diagram of εNd versus age for Tally Pond belt mudstone and volcanic rock samples from this study and from Rogers (2004), Rogers *et al*. (2006), and McNicoll *et al*. (2010). The field for Ganderian Neoproterozoic rocks is from Rogers *et al*. (2006). Fields for the Mesoproterozoic Amazonian crust, the Transamazonian crust, and the West African Craton are from Satkoski *et al*. (2010) and references therein. Depleted mantle evolution curve is from dePaolo (1981). CHUR = Chondrite uniform reservoir.

Table 1. *Sm-Nd isotope data for Lemarchant exhalites and bimodal volcanic rocks*

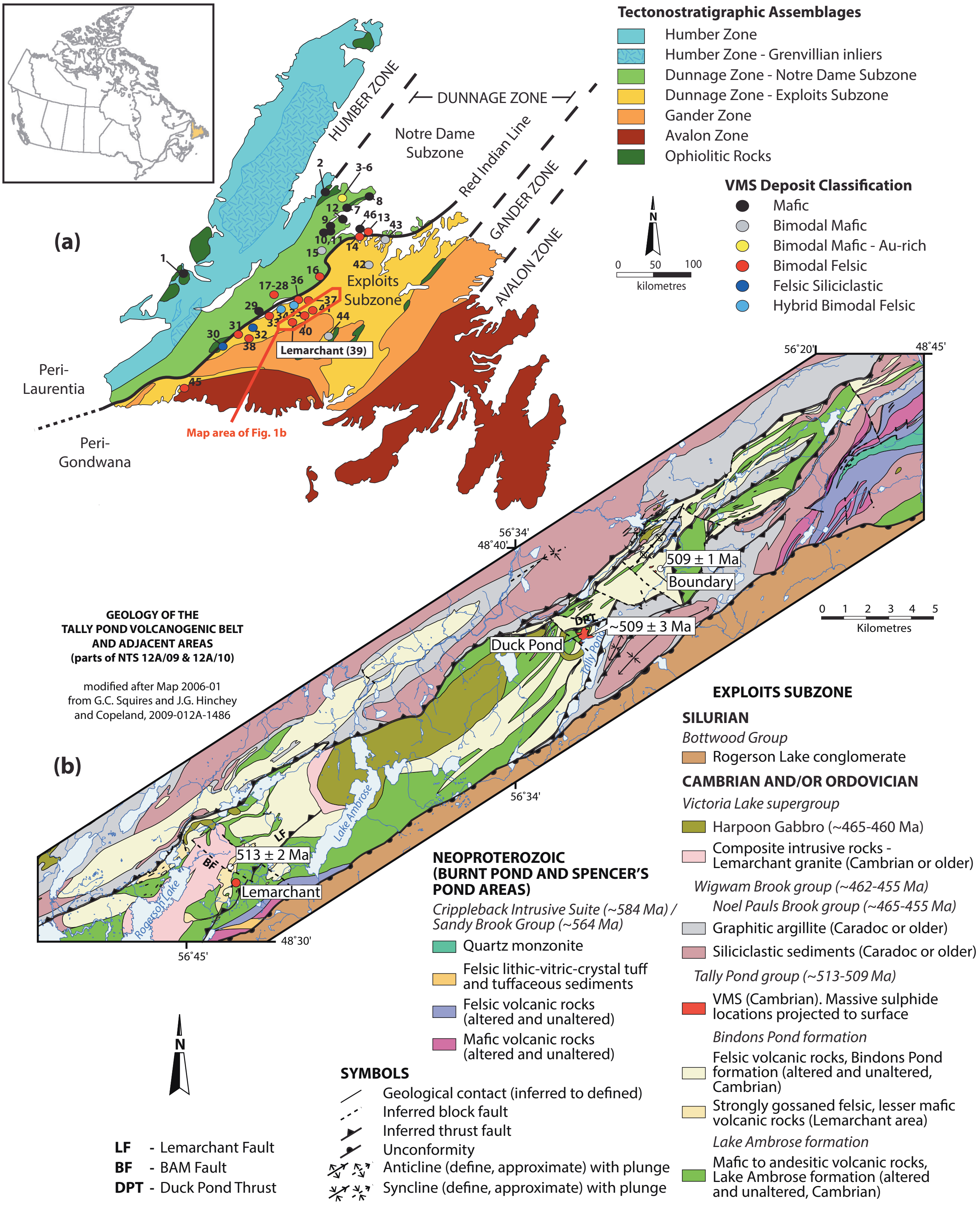
Sample #	Drill hole	Section (N)	UTM NAD27 Z21 - East	UTM NAD27 Z21 - North	Depth	Rock type	$^{143}Nd/^{144}Nd$ Rock t_0*	$^{147}Sm/^{144}Nd$ Rock t_0	$^{143}Nd/^{144}Nd$ Rock t_{513}	εNd_{513}	2σ‡	*f*Sm/Nd	T_{DM} [Ma]⊠
CNF-25062b	LM13-76	10050	5374537.00	521049.00	163.8	FEM	0.512206	0.129000	0.511772	-4.001	0.283	-0.344	1717.9
CNF-25065	LM13-77	10050	5374537.00	521049.00	140.0	Tuff	0.512161	0.126400	0.511736	-4.709	0.293	-0.357	1624.5
CNF-30982	LM11-65	10100	5374599.59	521114.13	157.7	EMS	0.512065	0.110900	0.511692	-5.567	0.286	-0.436	1809.6
CNF-38435	LM07-14	10200	5374697.64	521111.75	201.2	EMS	0.512213	0.133900	0.511763	-4.186	0.294	-0.319	1742.9
CNF-38433	LM07-14	10200	5374697.20	521114.68	503.5	IFE	0.512372	0.144700	0.511886	-1.789	0.278	-0.264	1702.6
CNF-20976	LM10-43	10250	5374724.55	520918.51	202.3	EMS	0.512134	0.121800	0.511725	-4.935	0.271	-0.380	1634.2
CNF-20995	LM07-15	10300	5374803.86	521072.26	174.0	IFE	0.512038	0.109000	0.511672	-5.970	0.317	-0.446	3047.8
CNF-30998	LM11-59	10325	5374828.82	521077.87	194.2	FEM	0.512404	0.176000	0.511813	-3.219	0.290	-0.105	2163.7
CNF-30953	LM07-17	10400	5374908.51	520989.96	238.4	EMS	0.512278	0.151600	0.511769	-4.078	0.278	-0.229	1698.4
CNF-20983	LM08-24	10500	5375010.66	521067.71	432.8	EMS	0.512122	0.120500	0.511717	-5.084	0.280	-0.387	1813.0
CNF-25002A	LM13-74	10600	5375124.00	520599.30	294.2	Tuff	0.512105	0.125000	0.511685	-5.711	0.288	-0.364	1816.2
CNF-20914	LM11-49	10800	5375314.26	521092.55	158.7	FEM	0.512231	0.135700	0.511775	-3.953	0.281	-0.310	1745.0
CNF-20910	LM11-49	10800	5375314.26	521092.55	144.6	Felsic	0.512477	0.142800	0.511997	0.386	0.293	-0.274	1472.3
CNF-20913	LM11-49	10800	5375314.26	521092.55	422.9	Mafic	0.512600	0.164400	0.512048	1.371	0.308	-0.164	1736.3

EMS = Exhalative mudstone immediately associated with massive sulphides (within 5m) and felsic and mafic volcanic rocks; FEM = Exhalative mudstone associated with felsic and mafic volcanic rocks; IFE = Interflow mudstone within mafic volcanic rocks.

*Calculated using $^{143}Nd/^{144}Nd$ of chondrite uniform reservoir (CHUR) = 0.512638 and $^{147}Sm/^{144}Nd$ CHUR today = 0.1967 from Rollinson (1993)

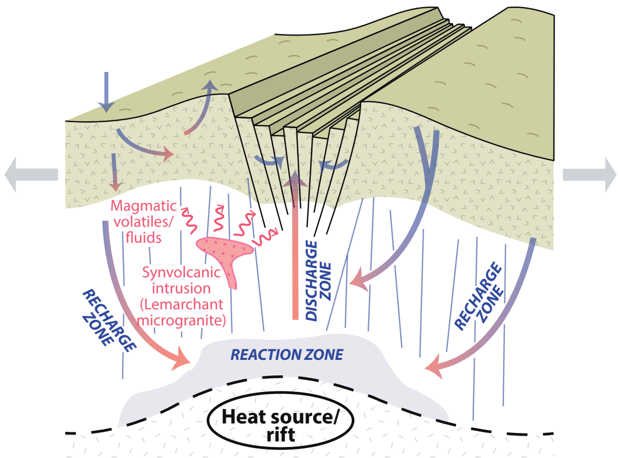
Calculated using the values of $^{143}Nd/^{144}Nd$ = 0.513163 and $^{147}Sm/^{144}Nd$ = 0.2137 for the depleted mantle reservoir (Goldstein et al.1984)

‡2σ calculated using the algorithm after Ickert (2013)



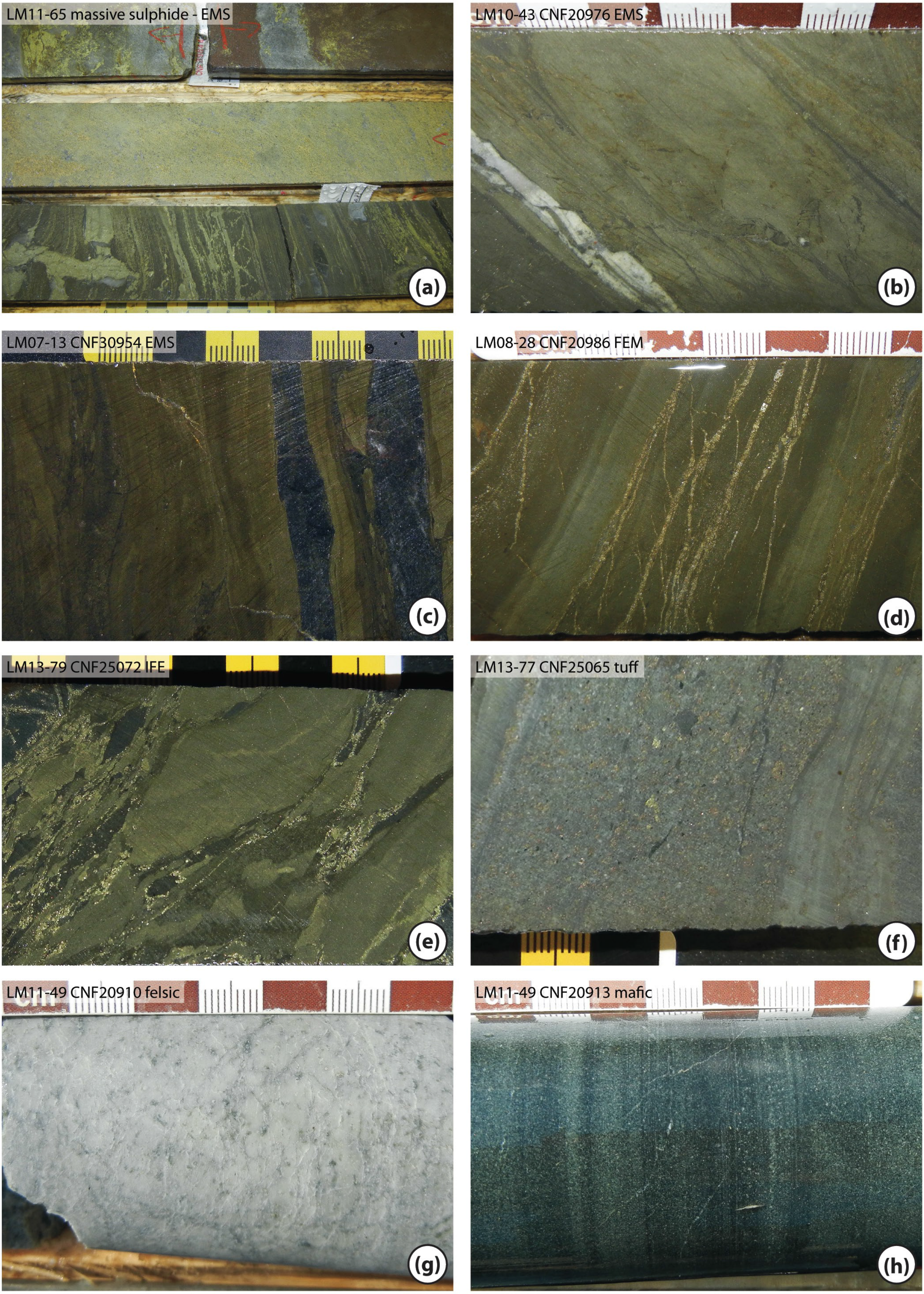
(a)
Tectonostratigraphic Assemblages
Humber Zone
Humber Zone - Grenvillian inliers
Dunnage Zone - Notre Dame Subzone
Dunnage Zone - Exploits Subzone
Gander Zone
Avalon Zone
Ophiolitic Rocks
VMS Deposit Classification
Mafic
Bimodal Mafic
Bimodal Mafic - Au-rich
Bimodal Felsic
Felsic Siliciclastic
Hybrid Bimodal Felsic
0 50 100
kilometres
HUMBER ZONE
DUNNAGE ZONE
Notre Dame Subzone
Red Indian Line
GANDER ZONE
AVALON ZONE
Exploits Subzone
Lemarchant (39)
Map area of Fig. 1b
Peri-Laurentia
Peri-Gondwana
(b)
GEOLOGY OF THE TALLY POND VOLCANOGENIC BELT AND ADJACENT AREAS (parts of NTS 12A/09 & 12A/10)
modified after Map 2006-01 from G.C. Squires and J.G. Hinchey and Copeland, 2009-012A-1486
56°20'
48°45'
56°34'
48°40'
509 ± 1 Ma
Boundary
~509 ± 3 Ma
Duck Pond
DPT
Tally Pond
Lake Ambrose
513 ± 2 Ma
LF
BF
Lemarchant
Rogerson Lake
48°30'
56°45'
0 1 2 3 4 5
Kilometres
EXPLOITS SUBZONE
SILURIAN
Bottwood Group
Rogerson Lake conglomerate
CAMBRIAN AND/OR ORDOVICIAN
Victoria Lake supergroup
Harpoon Gabbro (~465-460 Ma)
Composite intrusive rocks - Lemarchant granite (Cambrian or older)
Wigwam Brook group (~462-455 Ma)
Noel Pauls Brook group (~465-455 Ma)
Graphitic argillite (Caradoc or older)
Siliciclastic sediments (Caradoc or older)
Tally Pond group (~513-509 Ma)
VMS (Cambrian). Massive sulphide locations projected to surface
Bindons Pond formation
Felsic volcanic rocks, Bindons Pond formation (altered and unaltered, Cambrian)
Strongly gossaned felsic, lesser mafic volcanic rocks (Lemarchant area)
Lake Ambrose formation
Mafic to andesitic volcanic rocks, Lake Ambrose formation (altered and unaltered, Cambrian)
NEOPROTEROZOIC (BURNT POND AND SPENCER'S POND AREAS)
Crippleback Intrusive Suite (~584 Ma) / Sandy Brook Group (~564 Ma)
Quartz monzonite
Felsic lithic-vitric-crystal tuff and tuffaceous sediments
Felsic volcanic rocks (altered and unaltered)
Mafic volcanic rocks (altered and unaltered)
SYMBOLS
Geological contact (inferred to defined)
Inferred block fault
Inferred thrust fault
Unconformity
Anticline (define, approximate) with plunge
Syncline (define, approximate) with plunge
LF - Lemarchant Fault
BF - BAM Fault
DPT - Duck Pond Thrust

Fig. 2



Magmatic volatiles/ fluids
Synvolcanic intrusion (Lemarchant microgranite)
RECHARGE ZONE
DISCHARGE ZONE
RECHARGE ZONE
REACTION ZONE
Heat source/ rift

Fig. 3


LM11-65 massive sulphide - EMS
(a)
LM10-43 CNF20976 EMS
(b)
LM07-13 CNF30954 EMS
(c)
LM08-28 CNF20986 FEM
(d)
LM13-79 CNF25072 IFE
(e)
LM13-77 CNF25065 tuff
(f)
LM11-49 CNF20910 felsic
(g)
LM11-49 CNF20913 mafic
(h)

Lode, Stefanie Fig. 4

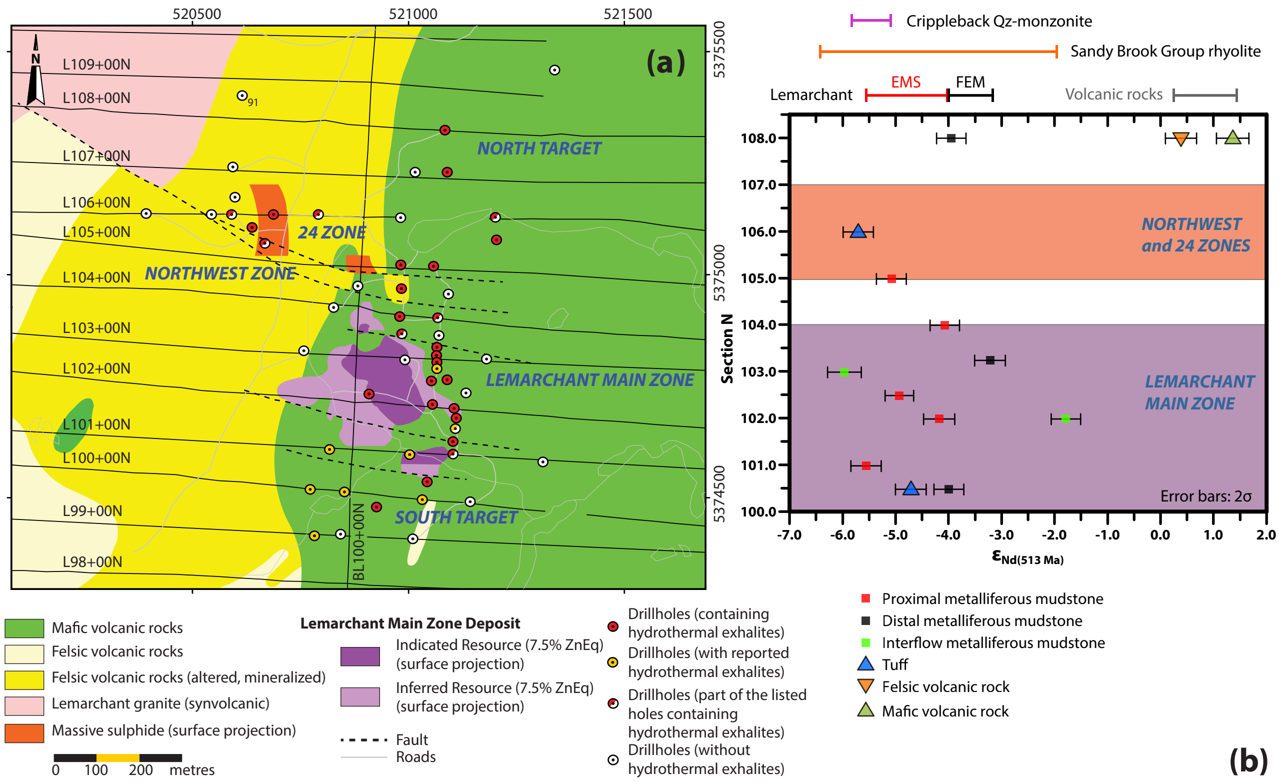
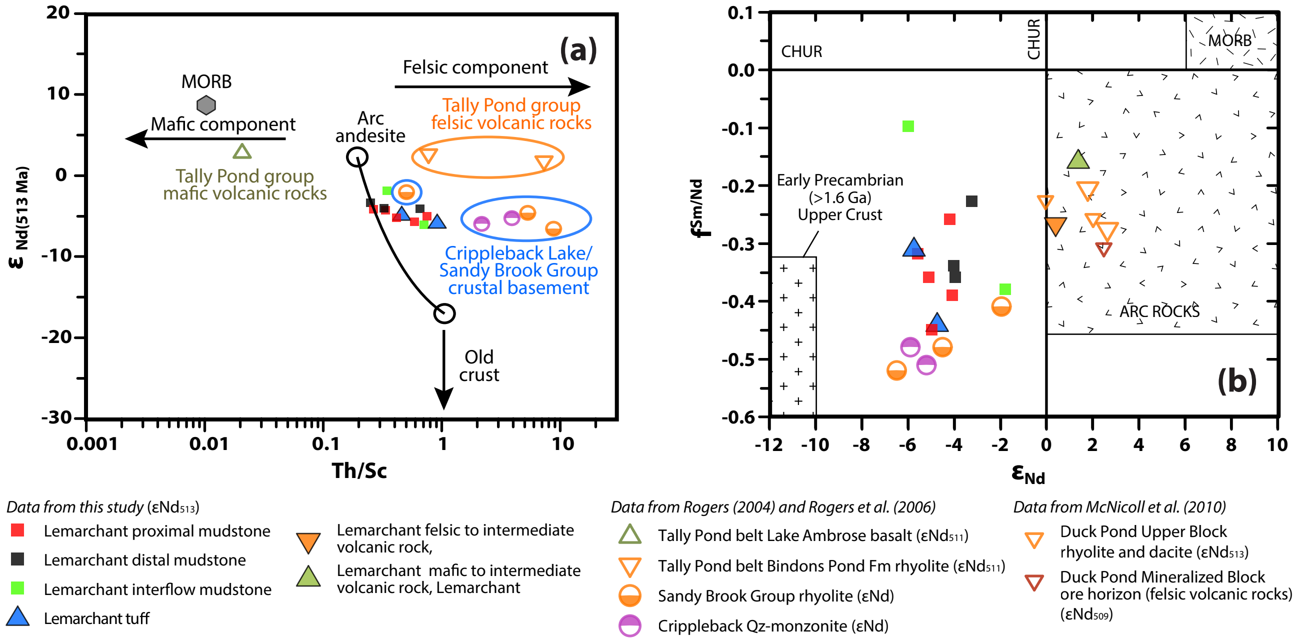
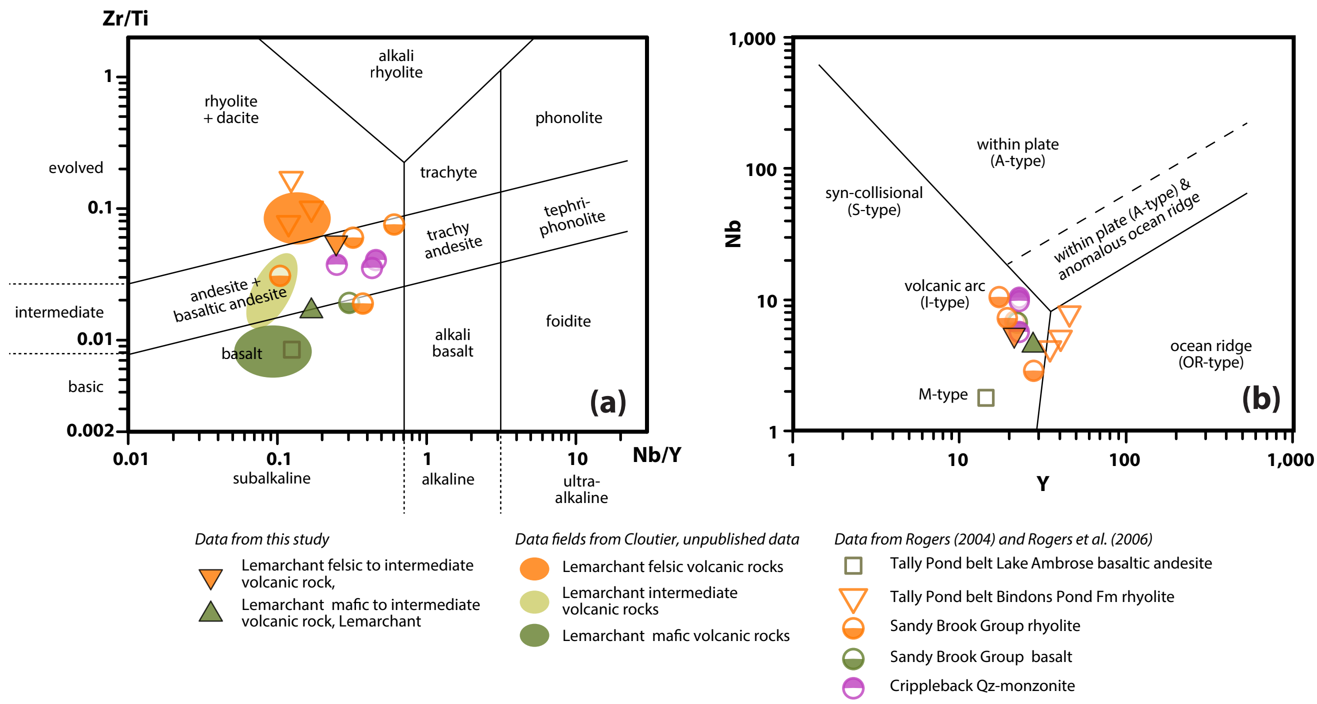


Fig. 5



(a)
MORB
Mafic component
Felsic component
Tally Pond group
mafic volcanic rocks
Arc
andesite
Tally Pond group
felsic volcanic rocks
Crippleback Lake/
Sandy Brook Group
crustal basement
Old
crust
ε Nd(513 Ma)
Th/Sc
20
10
0
-10
-20
-30
0.001
0.01
0.1
1
10
(b)
CHUR
MORB
Early Precambrian
(>1.6 Ga)
Upper Crust
ARC ROCKS
fSm/Nd
εNd
0.1
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-12
-10
-8
-6
-4
-2
0
2
4
6
8
10
Data from this study (εNd513)
Lemarchant proximal mudstone
Lemarchant distal mudstone
Lemarchant interflow mudstone
Lemarchant tuff
Lemarchant felsic to intermediate volcanic rock,
Lemarchant mafic to intermediate volcanic rock, Lemarchant
Data from Rogers (2004) and Rogers et al. (2006)
Tally Pond belt Lake Ambrose basalt (εNd511)
Tally Pond belt Bindons Pond Fm rhyolite (εNd511)
Sandy Brook Group rhyolite (εNd)
Crippleback Qz-monzonite (εNd)
Data from McNicoll et al. (2010)
Duck Pond Upper Block rhyolite and dacite (εNd513)
Duck Pond Mineralized Block ore horizon (felsic volcanic rocks) (εNd509)

Fig. 6


Zr/Ti
Nb/Y
rhyolite + dacite
alkali rhyolite
phonolite
trachyte
trachy andesite
tephri-phonolite
andesite + basaltic andesite
basalt
alkali basalt
foidite
evolved
intermediate
basic
subalkaline
alkaline
ultra-alkaline
(a)
Nb
Y
within plate (A-type)
syn-collisional (S-type)
within plate (A-type) & anomalous ocean ridge
volcanic arc (I-type)
ocean ridge (OR-type)
M-type
(b)
Data from this study
Lemarchant felsic to intermediate volcanic rock,
Lemarchant mafic to intermediate volcanic rock, Lemarchant
Data fields from Cloutier, unpublished data
Lemarchant felsic volcanic rocks
Lemarchant intermediate volcanic rocks
Lemarchant mafic volcanic rocks
Data from Rogers (2004) and Rogers et al. (2006)
Tally Pond belt Lake Ambrose basaltic andesite
Tally Pond belt Bindons Pond Fm rhyolite
Sandy Brook Group rhyolite
Sandy Brook Group basalt
Crippleback Qz-monzonite

Lode, Stefanie Fig. 7

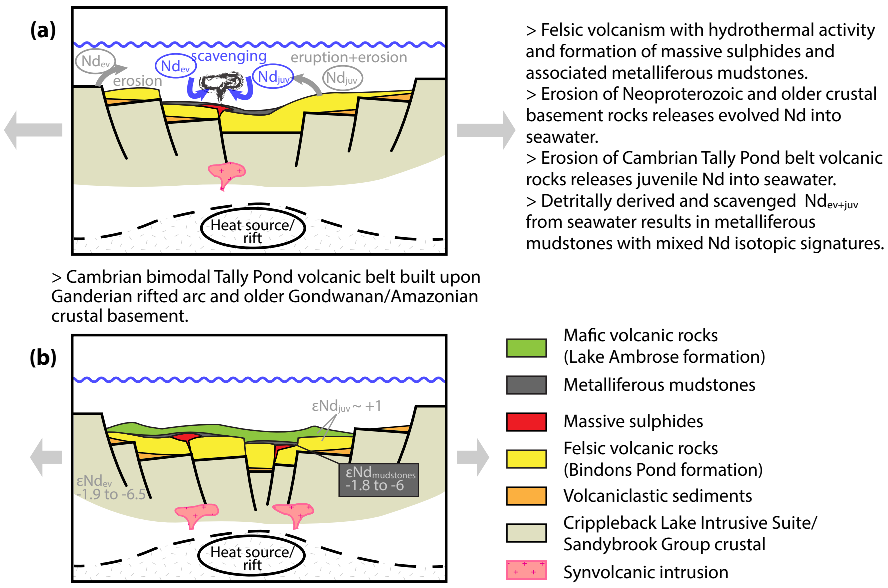
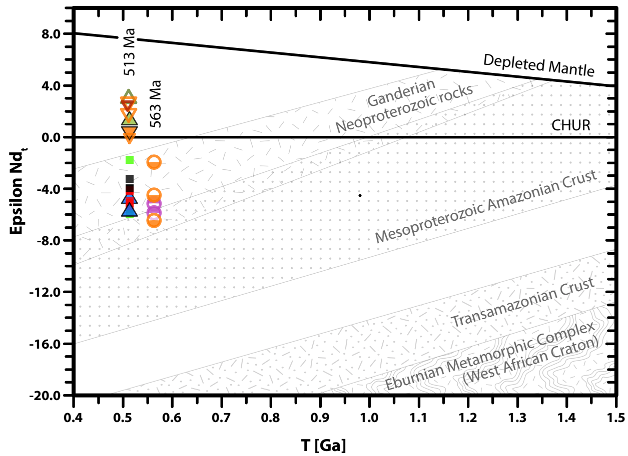


Fig. 8



Data from this study (εNd_{513})

- Lemarchant proximal mudstone
- Lemarchant distal mudstone
- Lemarchant interflow mudstone
- Lemarchant tuff
- Lemarchant felsic to intermediate volcanic rock,
- Lemarchant mafic to intermediate volcanic rock, Lemarchant

Data from Rogers (2004) and Rogers et al. (2006)

- Tally Pond belt Lake Ambrose basalt (εNd_{511})
- Tally Pond belt Bindons Pond Fm rhyolite (εNd_{511})
- Sandy Brook Group rhyolite (εNd)
- Crippleback Qz-monzonite (εNd)

Data from McNicoll et al. (2010)

- Duck Pond Upper Block rhyolite and dacite (εNd_{513})
- Duck Pond Mineralized Block ore horizon (felsic volcanic rocks) (εNd_{509})